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(54) ELECTROLYTE FILM AND ITS MANUFACTURING METHOD, AND FUEL CELL AND ITS
MANUFACTURING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a new electrolyte film, in which permeation of methanol (cross-over) is restrained as much as possible and which is also durable under an environment of higher temperature (not lower than about 130°C), and a fuel cell using the electrolyte film, especially methanol direct type solid polymer fuel cell, as well as to provide its manufacturing method.

SOLUTION: This electrolyte film, in which the first and the second polymers having a protonic conductivity are filled in fine pores of porous base material, which substantially does not swell with respect to methanol and water, and the electrolyte film where one end of the first polymer is made to be bonded to an inner surface of fine pores of the base material is used.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]Generally this invention relates to the electrolyte membrane for fuel cells, and more particularly the electrolyte membrane for direct type methanol polymer electrolyte fuel cells in detail about an electrolyte membrane. This invention relates to a fuel cell which has this electrolyte membrane, and a manufacturing method for the same.

[0002]

[Description of the Prior Art]The so-called prevention from discharge of greenhouse gases and NO_x is strongly cried for as the movement toward terrestrial environmental protection activates. In order to reduce the total emission of these gases, utilization of the fuel cell system for cars is considered to be very effective.

[0003]The polymer electrolyte fuel cell (PEFC, Polymer Electrolyte Fuel Cell) has the outstanding feature that only water is generated by low-temperature operation, high power density, and a power generation reaction. Especially, like gasoline, since it can supply as liquid fuel, it is thought that PEFC of methanol fuel is promising as power for electromobiles.

[0004]A polymer electrolyte fuel cell is classified into two types, the refining type which changes methanol into the gas of the hydrogen main ingredients using a reformer, and the direct type (DMFC, Direct Methanol Polymer Fuel Cell) which uses methanol directly without using a reformer. Since a type fuel cell has the directly unnecessary reformer, there is a big advantage of that the load change response which can be equal to frequent starting and stop so that a weight saving is possible is also substantially improvable, catalyst poisoning not becoming a problem, either, and the utilization is expected.

[0005]

[Problem(s) to be Solved by the Invention]However, some problems are pointed out to utilization of DMFC. For example, although DMFC uses a solid polymer electrolyte as an electrolyte, When the electrolyte membrane for ordinary PEFC, for example, the Nafion (registered trademark) film of Du Pont, the Dow film of Dow Chemical, etc. are used, Two big problems of the problem of dissolving near 130 ** if temperature is raised in order to raise the problem that a catalyst carries out depolarization and electromotive force declines in order that methanol may penetrate a film, and catalytic activity (creeping) occur. Although the electrolyte membrane which solves these problems simultaneously is not existing, if this problem is solved, the application to an electromobile may progress at a stretch.

[0006]Therefore, the purpose of this invention is to realize the new electrolyte membrane which controls the penetration (crossover) of methanol as much as possible, and is equal also to the use under elevated-temperature (not less than about 130 **) environment. The purpose of this invention is to provide the manufacturing method of the above-mentioned electrolyte membrane. The purpose of this invention is to realize the new methanol direct type solid polymer fuel cell which used the above-mentioned electrolyte membrane.

[0007]

[Means for Solving the Problem]In order to solve the above-mentioned problem, this invention persons acquired the following knowledge, as a result of repeating examination wholeheartedly. That is, generally, although polymer was softened at an elevated temperature, when the chemical bond of the temperature which carries out a pyrolysis was carried out and it embedded the 1st polymer into fine pores of a heat-resistant substrate paying attention to character to maintain the performance, knowledge that a skeleton of a substrate maintained a membranous structure also under an elevated temperature was acquired.

[0008]This invention persons acquired knowledge that proton conductivity could be improved, controlling a penetration (crossover) of methanol, when you made it filled up with the 2nd polymer in addition to the 1st polymer. While securing proton conductivity by polymer embedded into fine pores, shape maintenance under an elevated temperature, swelling control, and heat resistance acquired knowledge that a matrix of a porous substrate could attain.

[0009]From these knowledge, this invention persons found out the following inventions.

A process of forming the 1st polymer so that the end may be combined with a fine-pores internal surface of a porous substrate which has swelling-proof nature in <1> organic solvent and water, And a manufacturing method of an electrolyte membrane with which it is a manufacturing method of an electrolyte membrane which has a process which makes it filled up with the 2nd polymer that may be the same as the 1st polymer, or may differ in fine pores of said substrate, and said 1st and 2nd polymer has proton conductivity.

[0010]In <2> above <1>, the 1st polymer is of the 1st monomer origin, and it is good that the 2nd polymer is of the 2nd monomer origin that may be the same as the 1st monomer, or may differ.

In <3> above <1> or <2>, a formation process of the 1st polymer by having a process of irradiating a substrate with energy, and a process which contacts the 1st monomer to this substrate, and contacting the 1st monomer, It is good to form the 1st polymer so that the end may be combined with a fine-pores internal surface of a substrate.

[0011]An energy source of energy in <4> above <3> Plasma, It is chosen out of a group which consists of ultraviolet rays, an electron beam, and a gamma ray, excite a substrate according to this energy source, and by [of this substrate] generating the reaction starting point to a fine-pores internal surface at least, and contacting the 1st monomer at this reaction starting point, It is good to form the 1st polymer so that it may combine with a substrate in this reaction starting point.

In <5> above <1> or <2>, it is good for a formation process of the 1st polymer to combine an end of the 1st polymer with a substrate by a coupling agent.

[0012]In either of <6> above-mentioned <1>- <5>, it is good that it is a process which polymerizes the 2nd monomer with which it was filled up with the 2nd monomer like a packer of the 2nd polymer in fine pores of a substrate, and it this filled it up in fine pores, obtains the 2nd polymer, and is made by this to fill up with

inside of fine pores.

In either of <7> above-mentioned <1>- <6>, a porous substrate is good to comprise an inorganic material or heat-resistant polymer.

As for an inorganic material, in <8> above <7>, it is good that they are any one or those composite materials of ceramics, glass, or alumina.

[0013]In <9> above <7>, it is good that heat-resistant polymer is polytetrafluoroethylene or polyimide.

In either of <10> above-mentioned <1>- <9>, it is good that an electrolyte membrane is an electrolyte membrane for fuel cells.

In either of <11> above-mentioned <1>- <9>, it is good that an electrolyte membrane is an electrolyte membrane for direct type methanol solid polymer fuel cells.

[0014]It is an electrolyte membrane filling up fine pores of a porous substrate which does not swell substantially to <12> methanol and water with polymer which has proton conductivity, An electrolyte membrane which this polymer has the 1st proton conductive polymer and 2nd proton conductive polymer, and this 1st polymer is the polymer which combined the end with a fine-pores internal surface of said substrate, and is polymer which the 2nd polymer may be the same as the 1st polymer, or may differ.

[0015]In <13> above <12>, the 1st polymer is of the 1st monomer origin, and it is good that the 2nd polymer is of the 2nd monomer origin that may be the same as the 1st monomer, or may differ.

In <14> above <12> or <13>, after the 1st polymer irradiates a substrate with energy, it is good to be obtained by contacting the 1st monomer to this substrate.

[0016]An energy source of energy in <15> above <14> Plasma, It is chosen out of a group which consists of ultraviolet rays, an electron beam, and a gamma ray, excite a substrate according to this energy source, and by [of this substrate] generating the reaction starting point to a fine-pores internal surface at least, and contacting the 1st monomer at this reaction starting point, It is good to obtain the 1st polymer so that it may combine with said substrate in this reaction starting point.

In <16> above <12> or <13>, the 1st polymer is good to combine the end with a substrate by a coupling agent.

[0017]In either of <17> above-mentioned <12>- <16>, it is good to be filled up with the 2nd monomer in fine pores of a substrate, and to obtain the 2nd polymer by polymerizing the 2nd monomer with which it was this filled up in fine pores.

[0018]In either of <18> above-mentioned <12>- <17>, a porous substrate is good to comprise an inorganic material or heat-resistant polymer.

As for an inorganic material, in <19> above <18>, it is good that they are any one or those composite materials of ceramics, glass, or alumina.

[0019]In <20> above <18>, it is good that heat-resistant polymer is polytetrafluoroethylene or polyimide.

In either of <21> above-mentioned <12>- <20>, it is good that an electrolyte membrane is an electrolyte membrane for fuel cells.

In either of <22> above-mentioned <12>- <20>, it is good that an electrolyte membrane is an electrolyte membrane for direct type methanol solid polymer fuel cells.

[0020]A fuel cell in which it is a fuel cell in which <23> electrolyte membranes were formed on a cathode terminal or a catalyst bed of a cathode terminal, and this electrolyte membrane is one electrolyte membrane

of above-mentioned <12>- <22>.

[0021]Are an electrolyte inserted into <24> cathode poles, an anode pole, and these two poles a fuel cell which it has, and this electrolyte, It is an electrolyte filling up fine pores of a porous substrate which does not swell substantially to methanol and water with polymer which has proton conductivity, A fuel cell in which this polymer has the 1st proton conductive polymer and 2nd proton conductive polymer, and this 1st polymer is the polymer which combined the end with a fine-pores internal surface of said substrate and whose 2nd polymer is polymer which may be the same as the 1st polymer, or may differ.

[0022]In <25> above <24>, the 1st polymer is of the 1st monomer origin, and it is good that the 2nd polymer is of the 2nd monomer origin that may be the same as the 1st monomer, or may differ.

In <26> above <24> or <25>, after the 1st polymer irradiates a substrate with energy, it is good to be obtained by contacting the 1st monomer to this substrate.

[0023]An energy source of energy in <27> above <26> Plasma, It is chosen out of a group which consists of ultraviolet rays, an electron beam, and a gamma ray, excite a substrate according to this energy source, and by [of this substrate] generating the reaction starting point to a fine-pores internal surface at least, and contacting the 1st monomer at this reaction starting point, It is good to obtain the 1st polymer so that it may combine with a substrate in this reaction starting point.

In <28> above <24> or <25>, the 1st polymer is good to combine the end with a substrate by a coupling agent.

[0024]In either of <29> above-mentioned <24>- <28>, it is good to be filled up with the 2nd monomer in fine pores of a substrate, and to obtain the 2nd polymer by polymerizing the 2nd monomer with which it was this filled up in fine pores.

In either of <30> above-mentioned <24>- <29>, a porous substrate is good to comprise an inorganic material or heat-resistant polymer.

[0025]As for an inorganic material, in <31> above <30>, it is good that they are any one or those composite materials of ceramics, glass, or alumina.

In <32> above <30>, it is good that heat-resistant polymer is polytetrafluoroethylene or polyimide.

In either of <33> above-mentioned <24>- <32>, it is good that a fuel cell is a direct type methanol solid polymer fuel cell.

[0026]A process of applying <34> sol to the 1st pole, a process of using applied sol as a porous thin film layer, A process of filling up fine pores of an obtained porous thin film layer with a proton conductive polymer, and forming an electrolyte membrane on the 1st electrode, In a process of being a manufacturing method of a fuel cell which has a process at which the 2nd pole is stuck, and forming said electrolyte membrane on this electrolyte membrane, A manufacturing method of a fuel cell which said proton conductive polymer has the 1st and 2nd proton conductive polymers, and has a process of forming this 1st polymer so that an end of this 1st polymer may combine with the surface of said fine pores, and the process of being filled up with the 2nd polymer after formation of the 1st polymer.

[0027]In <35> above <34>, the 1st polymer and 2nd polymer may be the same, or may differ.

In <36> above <34> or <35>, the 1st polymer is of the 1st monomer origin, and it is good that the 2nd polymer is of the 2nd monomer origin that may be the same as the 1st monomer, or may differ.

[0028]In either of <37> above-mentioned <34>- <36>, after a formation process of the 1st polymer irradiates

a substrate with energy, it is good to be carried out by contacting the 1st monomer to this substrate.

[0029]An energy source of energy in <38> above <37> Plasma, It is chosen out of a group which consists of ultraviolet rays, an electron beam, and a gamma ray, excite a substrate according to this energy source, and by [of this substrate] generating the reaction starting point to a fine-pores internal surface at least, and contacting the 1st monomer at this reaction starting point, It is good to obtain the 1st polymer so that it may combine with a substrate in this reaction starting point.

In either of <39> above-mentioned <34>- <36>, it is good for a formation process of the 1st polymer to combine an end of the 1st polymer with a substrate by a coupling agent.

[0030]In either of <40> above-mentioned <34>- <39>, it is good to obtain the 2nd polymer by polymerizing the 2nd monomer that was filled up with the 2nd monomer in fine pores of a substrate, and was this filled up with it in fine pores.

In either of <41> above-mentioned <34>- <40>, a porous substrate is good to comprise an inorganic material or heat-resistant polymer.

[0031]As for an inorganic material, in <42> above <41>, it is good that they are any one or those composite materials of ceramics, glass, or alumina.

In <43> above <41>, it is good that heat-resistant polymer is polytetrafluoroethylene or polyimide.

[0032]In either of <44> above-mentioned <34>- <43>, it is good for the 1st pole to have the 1st support layer and 1st catalyst bed, and to apply said sol to said catalyst bed in a sol application process.

In either of <45> above-mentioned <34>- <44>, it is good to stick said electrolyte membrane and said 2nd catalyst bed in a process at which the 2nd pole has the 2nd support layer and 2nd catalyst bed, and sticks the 2nd pole.

[0033]In either of <46> above-mentioned <34>- <45>, it is good that a fuel cell is a direct type methanol solid polymer fuel cell.

[0034]

[Embodiment of the Invention]Hereafter, this invention is explained in detail. The electrolyte membrane of this invention has heat resistance, and the foam which does not swell substantially to an organic solvent and water, such as methanol, is used for it as a substrate. As a material with such character, there are ceramics, such as glass, alumina, or silica, etc. with an inorganic material. With other materials, polytetrafluoroethylene (for example, Teflon (registered trademark)), polyimide, etc. are mentioned. Such materials may be used independently or two or more sorts may be used for them as a composite material. When using as a composite material, more than two-layer may come to laminate the gestalt.

[0035]As for the void content of the substrate which can be used for this invention, it is suitably good that they are 10% - 95%. As for an average pore size, it is desirable that it is within the limits of 0.001 micrometer - 100 micrometers. As for the thickness of a substrate, it is preferably good that it is [of 100 micrometers or less] a several micrometers order.

[0036]The electrolyte membrane of this invention combines the 1st polymer, especially a graft polymer with the surface, especially the fine-pores internal surface of the substrate which consists of foam. This 1st polymer is of the 1st monomer origin, and the 1st monomer and 1st polymer have an ion exchange group. This 1st polymer, especially a graft polymer fill the inside of the fine pores of a substrate first. Since the 1st polymer is formed so that the end may combine with a fine-pores internal surface, this 1st polymer formed in

fine pores is not flowed out or eluted easily.

[0037]In this specification, as for an "ion exchange group", $-\text{SO}_3^-$ of $-\text{SO}_3\text{H}$ basis origin, etc. say the thing of the basis which holds and is easy to separate a proton, for example. When these exist in the 1st polymer in the shape of a pendant and this polymer fills the inside of fine pores, proton conductivity arises.

[0038]In order to form the 1st polymer so that the end may be combined with a fine-pores internal surface, there are the following methods. For example, a substrate is excited by plasma, ultraviolet rays, an electron beam, a gamma ray, etc., and it is the method of obtaining the 1st polymer, by [of this substrate] making a fine-pores internal surface generate the reaction starting point at least, and contacting the 1st monomer at this reaction starting point. The 1st polymer can also be combined with a fine-pores internal surface by the chemical methods, such as the Silang coupler. Fine pores are filled up with the 1st monomer, and after using the general polymerizing method for making a polymerization reaction perform by the inside, and obtaining the 1st polymer, the chemical bond of the 1st obtained polymer can be carried out to a substrate using the coupling agent which contains the above-mentioned Silang coupler etc., for example.

[0039]In this invention, it is preferred to use the plasma graft polymerization method explained below. That is, it is preferred to obtain the 1st polymer that was made to carry out the plasma graft polymerization reaction of the 1st monomer, and the end combined with the fine-pores surface. Plasma graft polymerization can be performed using the liquid phase process explained below and well-known gas phase polymerization process.

[0040]As for a monomer usable as the 1st monomer of this invention, acrylic sulfone sodium (SAS), sodium methallylsulfonate (SMS), p sodium styrenesulfonate (SSS), acrylic acid (AA), etc. are mentioned suitably. However, a monomer usable to this invention, Not the thing limited above but allylamine, allylsulfonic acid, Allylphosphonic acid, metallyl sulfonic acid, metallyl phosphonic acid, vinylsulfonic acid, Vinylphosphonic acid, styrene sulfonic acid, styrene phosphonic acid, the sulfonic acid of acrylamide, or a phosphonic acid derivative, Ethyleneimine, methacrylic acid, etc. may be derivatives, such as a monomer which has weak acid groups, such as strong acid groups, such as a vinyl group and sulfonic acid, and phosphonic acid, and a carboxyl group, the 1st class, the 2nd class, the 3rd class, a strong base like the 4th class amine, and a weak base in structure, and its ester. When the type of salts, such as sodium salt, is used as a monomer, after considering it as polymer, it is good to use those salts as a proton type etc.

[0041]A homopolymer may be formed using these monomers one sort, two or more sorts may be used and a copolymer may be formed. That is, the 1st polymer that the end combined with the surface in the fine pores of a substrate may be a homopolymer, or may be a copolymer.

[0042]The proton conductivity of an electrolyte membrane changes depending on the kind of the 1st monomer to be used and/or the 2nd monomer mentioned later. Therefore, it is desirable to use a monomer material with high proton conductivity. It depends for electrolytic proton conductivity also on the degree of polymerization of the polymer which fills the inside of fine pores.

[0043]In this invention, proton conductivity is given by being formed and/or filled up with the 1st polymer and the 2nd polymer mentioned later in fine pores. Therefore, it is good for both sides to have a high degree of polymerization, or for the 1st polymer and 2nd polymer to crawl, and for a gap or one side to have a high degree of polymerization. It is good for the 2nd polymer to have a high degree of polymerization on

manufacturing efficiency especially. Or although both sides do not have a high degree of polymerization relatively, it is good by combining both sides for each to have a degree of polymerization of the grade which has high proton conductivity.

[0044]Plasma graft polymerization method usable to manufacture of the electrolyte membrane of this invention, After irradiating a substrate with plasma and making a base material surface and a fine-pores internal surface generate the reaction starting point, it is made to contact by the method of a liquid phase polymerization common knowledge of the 1st monomer suitably, and the graft polymerization of the 1st monomer is carried out in the inside of a base material surface and fine pores.

[0045]It explains in detail, referring to drawings for plasma graft polymerization method usable to this invention next. The detailed contents of plasma graft polymerization method are explained also to the precedence application by the artificers of this invention, JP,3-98632,A, JP,4-334531,A, JP,5-31343,A, JP,5-237352,A, and JP,6-246141,A in detail.

[0046]Drawing 1 is a partial section perspective view showing the porous substrate 1 usable to the electrolyte membrane of this invention. To the porous substrate 1, the fine pores 2 which penetrate a substrate are opening many.

[0047]Frequency of 10-50 MHz is performed to the porous substrate 1 under existence of the gas by which a pressure range serves as 120kPa from 1mPa, such as argon, nitrogen, and air, and plasma treatment for about 1 to 1000 seconds is usually performed with the outputs 1-1000W. The reaction starting point (not shown) occurs in the surface (a fine-pores internal surface is also included) of the substrate 1 put to plasma at this time.

[0048]Next, the 1st monomer that has an ion exchange group is dissolved in water, and the homogeneous solution of the 1st monomer is prepared. As for the concentration of the solution of the 1st monomer, it is preferably desirable to carry out to 1 to 10% of the weight 0.1 to 80% of the weight. The homogeneous solution of the 1st monomer may have the surface-active agent, for example, dodecylbenzenesulfonic acid etc., so that this solution may permeate easily into fine pores. The surface-active agent may be contained in this 2nd monomer solution when using the 2nd monomer solution.

[0049]The substrate 1 after plasma treatment is good to process as follows with the solution of the 1st monomer of the above. That is, the 1st monomer aqueous solution is made to contact directly under argon gas atmosphere. Or the substrate 1 is once taken out in the air and the point which was made to react to oxygen and carried out activity by plasma is changed into a peroxide group. Then, the substrate 1 which has a peroxide group is contacted to the 1st monomer aqueous solution. Contact is performed by more specifically immersing the porous substrate 1 which the reaction starting point has generated in the above-mentioned solution. When carrying out directly under argon gas atmosphere, it is good to perform 20 ** - 100 ** at the temperature of 30-60 ** preferably, and this process is good to carry [60 ** - 150 **] out at 80 ** - 120 ** preferably, when generating a peroxide group. Immersion is good to carry out carrying out bubbling with inactive gas, such as nitrogen gas. As for time to be immersed, it is good the day grade from 1 minute and that they are 1 hour - 24 hours preferably.

[0050]Next, the porous predetermined substrate 1 which carried out time progress is pulled up from solution, and is washed and dried by organic solvents, such as toluene or xylene. This is for flushing thoroughly the homopolymer etc. which were secondarily generated in process of the polymerization by an organic solvent,

and leaving a graft polymer only to the substrate fine-pores surface and an inside.

[0051] Drawing 2 is a perspective view showing notionally the state where the monomer carried out graft polymerization in the substrate 1. It turns out that the 1st polymer 3 that carried out graft polymerization is formed in the inside not only of the surface of a substrate but the fine pores 2.

[0052] Thus, the substrate with which the 1st polymer was formed so that the end might be combined with the fine-pores surface of a porous substrate is obtained. In this invention, it is filled up with the 2nd polymer in the fine pores of the substrate produced by ranking second. As for the 2nd polymer, it is good that it is polymer which has proton conductivity. That is, like the 1st above-mentioned polymer, as long as it is polymer which has an ion exchange group, it may be the same as the 1st polymer, or may differ.

[0053] A method that the filling method of the 2nd polymer is directly filled up with the 2nd polymer in fine pores, And after being filled up with the 2nd monomer that serves as the 2nd polymer by subsequent processing in fine pores, a polymerization reaction is performed within these fine pores, the 2nd polymer is obtained, and there are a method etc. which are filled up with the 2nd polymer in fine pores by this.

[0054] When using the 2nd monomer, the 2nd monomer may be the same as the 1st monomer, or may differ. That is, what chose one sort or two sorts or more from the 1st monomer illustrated above can be used. As the 2nd suitable monomer, what was mentioned above as the 1st monomer is mentioned, and, in addition to this, vinylsulfonic acid can be mentioned. When one sort is chosen as the 2nd monomer, the 2nd polymer is a homopolymer, and the 2nd polymer is a copolymer when two or more sorts are chosen as the 2nd monomer.

[0055] As for the 2nd polymer, it is preferred the 1st polymer, a chemical bond, and/or to carry out physical combination. For example, the whole of the 2nd polymer may be carrying out the chemical bond to the 1st polymer, or the whole of the 2nd polymer may be carrying out physical combination with the 1st polymer. A part of 2nd polymer is carrying out the chemical bond to the 1st polymer, and the other 2nd polymer may be carrying out physical combination with the 1st polymer. Combination with the 1st polymer and the 2nd polymer is mentioned as a chemical bond. This combination can be formed, when the reactant group is made to hold to the 1st polymer for example and this reactant group, the 2nd polymer, and/or the 2nd monomer react. The state where the 1st and 2nd polymer becomes entangled is mentioned as a state of a physical combination, for example.

[0056] Proton conductivity can be improved in this invention, without the whole polymer with which it was filled up in fine pores eluting or flowing out of the inside of fine pores, controlling the penetration (crossover) of methanol by using the 1st and 2nd polymer together. The whole polymer with which the 1st polymer and 2nd polymer were especially filled up in fine pores a chemical bond and/or by carrying out physical combination does not elute or flow out of the inside of fine pores. Even if it is when the degree of polymerization of the 1st polymer is low, when the 2nd polymer, especially the 2nd polymer with a high degree of polymerization exist, the proton conductivity of the electrolyte membrane obtained can be improved.

[0057] Hereafter, the filling method of the 2nd polymer is briefly explained using drawing 3. Drawing 3 (a) is a figure showing the section of the fine pores typically about the substrate after the 1st polymer was formed. In drawing 3 (a), the same drawing number as drawing 2 is used, the fine pores 2 are formed in the substrate 1, and the 1st polymer 3 is formed so that the end may combine with the surface of the fine pores 2.

[0058] Thus, the fine pores of the substrate with which the 1st polymer is formed are filled up with the 2nd monomer, and a polymerization reaction is performed within these fine pores. It is shown that the 2nd polymer 5 obtained by the polymerization reaction is filled up with drawing 3 (b) in fine pores. as mentioned above, the 2nd polymer 5 -- the 1st polymer 3 and a chemical bond -- and/or, physical combination is carried out, and the 2nd polymer 5 as well as the 1st polymer is not easily flowed out or eluted out of fine pores.

[0059] In the electrolyte membrane or the fuel cells, and those manufacturing methods of this invention, the 3rd polymer, the 4th polymer, ..., the n-th polymer (namely, n three or more integers) can be used. The n-th polymer may have the operation which improves proton conductivity like the 2nd polymer. Even if it has the operation which prevents flowing out or eluting the whole polymer from the fine pores of a substrate, the n-th polymer may be constituted so that it may have the other character needed for a fuel cell.

[0060] As for the electrolyte membrane of this invention, it is preferred to use for the methanol fuel cell containing a fuel cell especially a direct type methanol solid polymer fuel cell, or a refining type methanol solid polymer fuel cell. As for the electrolyte membrane of this invention, it is preferred especially to use for a direct type methanol solid polymer fuel cell.

[0061] Here, the composition of a methanol fuel cell is explained briefly, referring to drawing 4. Drawing 4 is a schematic diagram showing one mode of the methanol fuel cell which uses the electrolyte membrane of this invention.

[0062] The methanol fuel cell 11 has the electrolyte 17 inserted into the cathode pole 13, the anode pole 15, and these two poles. A methanol fuel cell has a reformer which is not illustrated in the anode electrode side, and is good also as a refining type methanol fuel cell.

[0063] It becomes impossible to have a support layer which can consider a cathode pole as composition more publicly known than before, for example, supports a catalyst bed and this catalyst bed sequentially from the electrolyte side. It becomes impossible to have a support layer which can also consider an anode electrode as composition more publicly known than before, for example, supports a catalyst bed and this catalyst bed sequentially from the electrolyte side.

[0064] After carrying out integral moulding of the 1st pole and electrolyte and acquiring a Plastic solid, the methanol fuel cell which has an electrolyte of this invention can also be obtained by the ability to stick this Plastic solid and the 2nd pole so that a different catalyst bed of the 2nd pole from the 1st pole and this electrolyte side may stick.

[0065] The case where the 1st pole is a cathode pole is explained using drawing 5. Drawing 5 is a schematic diagram showing one mode of a cathode pole which uses the electrolyte membrane of this invention. The cathode pole 13 has the catalyst bed 21 on the support layer 19 among drawing 5. As for this support layer 19, it is preferred to consist of what has gas permeation nature especially oxygen permeability, heat resistance, and electron conductivity. For example, it is good that it is porous carbon and is what has electron conductivity.

[0066] The catalyst bed 21 is a layer which supports a catalyst more publicly known than the former [****] to the cathode pole. On this catalyst bed 21, the porous thin film 23 which has the fine pores 2 as shown in drawing 1 is formed. In formation of a porous thin film, the sol which serves as various glass, such as an alkoxide of various silicon, an alkoxide of various aluminum, an alkoxide of various titanium, or an alkoxide of various zirconiums, or ceramics, for example is prepared, and this sol is applied to a catalyst bed. A method

more publicly known than the former, such as dip coating, spin coating, and spray coating, can be used for the applying method. Thus, the applied sol is warmed by desiccation and request and a porous thin film is obtained. As for the porous thin film obtained, it is good that it is a thin film of silica, alumina (for example, gamma-alumina), a titania, zirconia, these mixtures, or a complex.

[0067]In the fine pores of the obtained porous thin film, by the 1st above-mentioned polymer, for example, graft polymerization method, or the method of using a coupling agent, the 1st polymer is formed so that the end of this 1st polymer may combine with a fine-pores internal surface. Subsequently, it is filled up with the 2nd polymer in fine pores by an above-mentioned method. Thus, a cathode pole and an electrolyte can carry out integral moulding. By using such an integral-moulding object, handling of the thin-film-ized electrolyte membrane becomes easy.

[0068]Adhesion shaping can be carried out and a methanol fuel cell can be formed so that the electrolyte side of a Plastic solid may stick this Plastic solid and an anode pole the catalyst bed side of an anode pole. In ****, although how to carry out integral moulding of a cathode pole and the electrolyte was described, if it is also a person skilled in the art to carry out integral moulding of an anode pole and the electrolyte, it can think out easily from ****.

[0069]

[Example]Although this invention is explained in more detail based on an example, this invention is not limited to this example.

(Example 1) The porous PTFE film (trademark Teflon, the NITTO DENKO make, flat films, 70 micrometers in thickness, pore diameter of 50 nm) was used as a substrate. The substrate concerned was washed and plasma irradiation was performed on condition of the following.

[0070]High frequency output: 30W;

Plasma-irradiation time: For 60 seconds;

Atmosphere: Argon gas;

Pressure: 10 Pa.

[0071]The substrate after plasma irradiation was immersed in the 1st monomer solution that carried out freezing deaeration, and graft polymerization was performed. Graft polymerization conditions are shown below.

[0072]Monomer: Acrylic acid (AA);

Monomer concentration: 10 % of the weight;

Solvent: Water;

Temperature: About 60 **;

time: -- 10 to 24 hour,; and additive agent: -- a surface-active agent (sodium dodecylbenzenesulfonate).

[0073]After pulling up the porous substrate from the solution and washing it underwater, the film A-1 which made it dry and formed the 1st polymer was obtained. The mass of the film A-1 was measured after desiccation, and the amount of graft polymerization was calculated as compared with the mass before a polymerization. The amount of graft polymerization was 0.7 mg/cm^2 . Incidentally, the film pressure after a polymerization was about 90 micrometers.

[0074]In this way, when FT-IR (Mapping method) measurement of the obtained film A-1 was carried out, it

was checked that the peak of 1740 cm^{-1} of a carboxyl group exists also inside membranous, and it became clear that polymer was formed also in the inside of membranous.

[0075]It <restoration of the 2nd polymer> Ranked second and was filled up with the 2nd polymer. Acrylic acid (AA) was used like the 1st polymer as the 2nd monomer. The 2nd monomer 98.9 weight section and the 2nd monomer solution that consists of divinylbenzene 0.1 weight section and water-soluble azo polymerization initiator 1.0 weight section as a cross linking agent were prepared. The film A-1 obtained above was immersed in this 2nd polymer solution.

[0076]It irradiated with visible light for 6 minutes after immersion, and the thermal polymerization reaction was made to perform inside fine pores. Then, the film A-2 which backwashing by water of the obtained film is carried out in an ultrasonic wave, and it dried and was made to fill up with the 1st and 2nd polymer was obtained. The difference of the weight before and behind restoration of the 2nd polymer showed that a lap was 7.0 mg/cm^2 .

[0077](Example 2) Using the mixture of acrylic acid (AA):vinylsulfonic acid =2:1 as the 2nd monomer, in order to dissolve vinylsulfonic acid, the film A-3 was obtained by the same method as Example 1 except having used the water of certain quantity.

[0078](Example 1 of reference) The film A-4 filled up only with the 1st polymer as well as the film A-1 of Example 1 was obtained. However, the lap of the film A-4 was 3.0 mg/cm^2 .

[0079]<Proton conductivity measurement> The proton conductivity was measured about the obtained film A-2 to A-4. When measuring, the film was swollen underwater, it inserted into the stainless steel foil electrode after that first, and the proton conductivity test sample was produced. About these samples, impedance measurement was performed by HP4192A by Hewlett Packard. The obtained result is shown below.

[0080]Film A-4(example 1 of reference): $0.04\times 10^{-2}\text{ S/cm}$;

Film A-2(example 1): $0.10\times 10^{-2}\text{ S/cm}$; and film A-3(example 2): $0.62\times 10^{-2}\text{ S/cm}$.

[0081]Thus, high proton conductivity was able to be acquired by being filled up with the 2nd polymer. Each of films A-2 and A-3 had desired heat resistance and the methanol inhibition performance. That is, it turned out that the electrolyte membrane A-2 of this example and A-3 have the low permeability of methanol, and heat-resistant and high proton conductivity.

[0082]

[Effect of the Invention]The new electrolyte membrane which controls the penetration (crossover) of methanol as much as possible, and is equal also to the use under elevated-temperature (not less than about 130°C) environment by this invention can be provided. In addition to the above-mentioned effect besides the above-mentioned effect, the method of manufacturing the above-mentioned electrolyte membrane is provided by this invention, but it can do. In addition to the above-mentioned effect besides the above-mentioned effect, the new methanol direct type solid polymer fuel cell using the above-mentioned electrolyte membrane can be provided by this invention.

[Translation done.]

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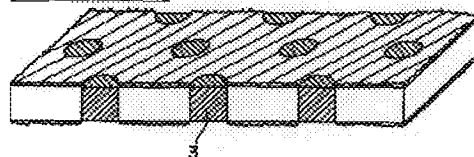
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DRAWINGS

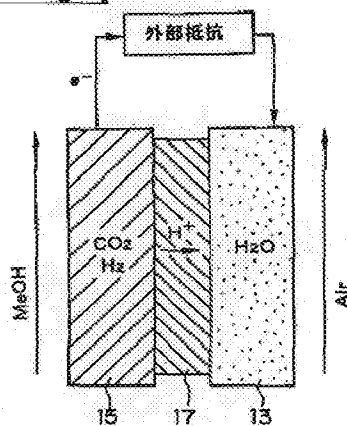
[Drawing 1]



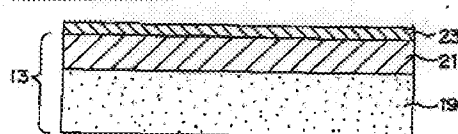
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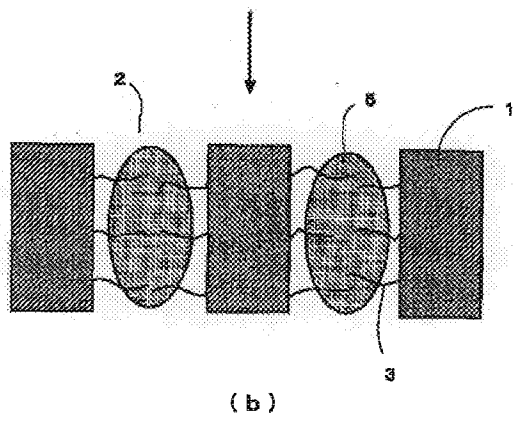
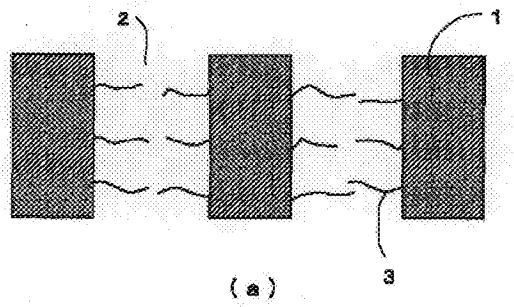
[Drawing 4]



[Drawing 5]



[Drawing 3]



[Translation done.]